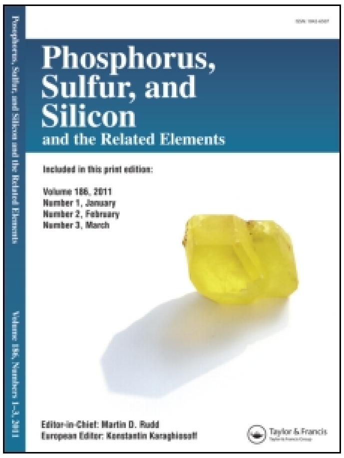

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GEOMETRICAL FACTORS AFFECTING THE STABILITY OF SULFONIUM YLIDES. AN EXPERIMENTAL STUDY AND A MO RATIONALIZATION OF THE KINETIC ACIDITY OF DIASTEREOTOPIC PROTONS ALPHA TO -$S^+R_1R_2$

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GEOMETRICAL FACTORS AFFECTING THE STABILITY OF SULFONIUM YLIDES. AN EXPERIMENTAL STUDY AND A MO RATIONALIZATION OF THE KINETIC ACIDITY OF DIASTEREOTOPIC PROTONS ALPHA TO $-S^{+}R_1R_2$.

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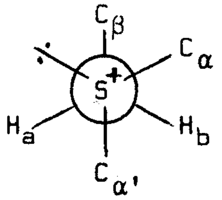
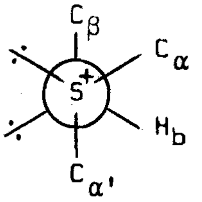
A recent study[1] of the reactivity (H-D base-catalyzed exchange) of diastereotopic α sulfonium protons, $C_{\alpha}C_{\alpha'}S^{+}\text{-}C(H_aH_b)\text{-}$, has suggested an important geometrical factor contributing to the stability of the quasi-ylide transition state. This is the syn or anti alignment of the incipient lone pair orbital with one of the adjacent $S^{+}\text{-}C_{\alpha}$ bonds. Thus, for example, of the ylides derived from A, a rigid sulfonium precursor, B (lone pair anti to C_{α}) appears to be more stable than C (lone pair gauche to both C_{α} and $C_{\alpha'}$). A MO study suggests the stabilizing factor in question is due to the orbital interaction between the lone pair group orbital and the σ^{*} group orbital of the adjacent $S^{+}\text{-}C_{\alpha}$ bond, the interaction being at a maximum when the orbitals involved are either syn or anti coplanar.



A



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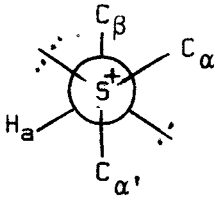
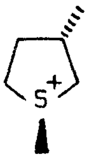


C

For testing the theory and establishing the relative importance of this and other steric and/or electronic factors, the 5-membered cyclic sulfonium cations appeared to be most suitable by virtue of their especially large diastereotopic reactivity differentials.[2]

We have therefore considered the series of thiolanium cations 1-4 below, characterized by an increasing conformational bias, and have: a) studied the conformational properties in solution by high



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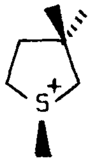

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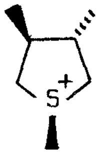

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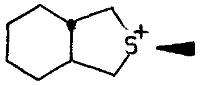

4

field ^{1}H and ^{13}C NMR; b) determined, for each compound, the kinetic acidity of their four diastereotopic endocyclic α protons; c) determined the molecular geometry (X-Ray) of the rigid cation 4, and d) used this geometry to compute, by an ab initio MO approach, the stability of the four diastereomeric ylides derived from 4, together with the barriers to pyramidal inversion of both endocyclic α-carbanions.

The results of this study confirm the major stabilizing factor of the ylide is related to the postulated orbital interaction between the carbanion lone pair orbital and the antibonding σ^* group orbital of the adjacent S^+-CH_3 bond.

1. G. Barbarella, P. Dembech, A. Garbesi, F. Bernardi, A. Bottoni, and A. Fava, J.Amer.Chem.Soc., 99, December 1977.

2. G. Barbarella, A. Garbesi, and A. Fava, J.Amer.Chem.Soc., 97, 5883 (1975).